

**OH from peroxy  
radicals**

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# Direct detection of OH formation in the reactions of HO<sub>2</sub> with CH<sub>3</sub> C(O)O<sub>2</sub> and other substituted peroxy radicals

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## Abstract

This work details the first direct observation of OH as a product from (R1):  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow$  (products), which has generally been considered an atmospheric radical termination process. The technique of pulsed laser photolysis radical generation, coupled to calibrated laser induced fluorescence detection was used to measure an OH product yield for (R1) of  $\alpha_1 = (0.5 \pm 0.2)$ . This study of (R1) included the measurement of a rate coefficient  $k_1(298 \text{ K}) = (1.4 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , substantially reducing the uncertainties in modelling this important atmospheric reaction. OH was also detected as a product from the reactions of  $\text{HO}_2$  with three other carbonyl-containing peroxy radicals, albeit at smaller yield, e.g. (R2):  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow$  (products),  $\alpha_2 \approx 0.15$ . By contrast, OH was not observed ( $\alpha < 0.06$ ) as a major product from reactions where carbonyl functionality was absent, e.g.  $\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2$  (R8), and  $\text{HO}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2$  (R9).

## 1 Introduction

The hydroxyl radical, OH, is the primary oxidant in the Earth's atmosphere, initiating the degradation of common trace gases such as  $\text{CH}_4$ , CO and the important non-methane hydrocarbon (NMHC) isoprene ( $\text{C}_5\text{H}_8$ , 2-methyl-1,3-butadiene) (Atkinson and Arey, 2003). Key intermediates in the atmospheric oxidation of NMHC are the hydroperoxyl radical,  $\text{HO}_2$ , and organic peroxy radicals,  $\text{RO}_2$  (Lightfoot et al., 1993; Tyndall et al., 2001). The reactions between  $\text{HO}_2$  and  $\text{RO}_2$  have long been of interest to atmospheric scientists as they are important radical termination processes, inhibiting  $\text{O}_3$  and OH generation, and producing phytotoxic organic hydrogen peroxides, ROOH, and peracids,  $\text{RC}(\text{O})\text{OOH}$ . Recent experimental and theoretical work has, however, suggested that the reactions of  $\text{HO}_2$  with some substituted  $\text{RO}_2$ , do not exclusively terminate radical chemistry. For the reaction (R1) of  $\text{HO}_2$  with acetyl peroxy,  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , Hasson and co-workers reported a significant yield of OH radicals (R1c) (Hasson et

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al., 2004), in addition to the well-established radical terminating peracid (R1a) and O<sub>3</sub> (R1b) products (Niki et al., 1985; Moortgat et al., 1989; Horie and Moortgat, 1992; Crawford et al., 1999; Tomas et al., 2001).



The OH or CH<sub>3</sub>C(O)O radical products (R1c) were not directly detected, but rather FTIR and HPLC end-product analysis (in particular of CH<sub>3</sub>OOH produced in a series of reactions following CH<sub>3</sub>C(O)O decomposition) was used (Hasson et al., 2004) to derive an OH product yield,  $\alpha_1 \equiv k_{1c}/k_1 = (0.4 \pm 0.16)$ . The authors noted that OH generation in (R1c) may have caused a serious (factor of  $\approx 2$ ) underestimation in previous determinations of the overall rate coefficient,  $k_1$ . Depending on experimental conditions, the OH products could recycle HO<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub>, essentially leaving kinetic experiments blind to (R1c).

Reaction (R1) was subsequently studied in two independent laboratories, both using an OH scavenger (benzene) to trap any OH products. From the results of new real-time experiments, a re-analysis of previously published kinetic data, and a theoretical treatment of (R1), Le Crâne et al. assigned an upper-limit of  $\alpha_1 < 0.1$  (Le Crane et al., 2006) and concluded that (R1) is, as previously thought, predominantly a radical termination process. By contrast, Jenkin and co-workers did obtain evidence for a significant propagation (R1c) channel from their FTIR end-product analysis (Jenkin et al., 2007). Based largely upon yields of phenol (produced from C<sub>6</sub>H<sub>6</sub>+OH in air) Jenkin et al. obtained  $\alpha_1 = (0.43 \pm 0.1)$ , in excellent agreement with the results of Hasson et al. It was suggested that Le Crâne et al. had overestimated the stability of HOC<sub>6</sub>H<sub>6</sub> radicals (formed from C<sub>6</sub>H<sub>6</sub>+OH) used as the diagnostic for OH, and so underestimated the importance of channel (R1a). (Jenkin et al., 2007)

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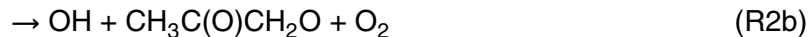
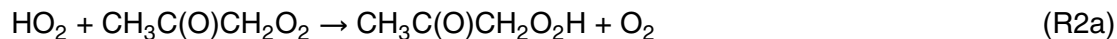
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Note that none of these three studies (Hasson et al., 2004; Le Crane et al., 2006; Jenkin et al., 2007) could directly detect OH as product from (R1). Clearly there remain large uncertainties in both  $\alpha_1$  and  $k_1$ . The principal aim of the work presented in this manuscript was therefore to unambiguously identify any OH produced in (R1), and so to reduce uncertainties in the two important atmospheric parameters  $\alpha_1$  and  $k_1$ .

There are indications in the literature that other naturally occurring, substituted RO<sub>2</sub> may react with HO<sub>2</sub> to produce significant OH products. A large  $\alpha_2=(0.69\pm 0.2)$  was reported for the reaction (R2) of HO<sub>2</sub> with acetyl peroxy, CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> (Hasson et al., 2004):



By contrast, no evidence for OH production was obtained from the reaction of HO<sub>2</sub> with the non-substituted C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> radical. In a subsequent quantum chemical/master equation study, it was demonstrated that hydrogen bonding to the carbonyl group of CH<sub>3</sub>C(O)O<sub>2</sub> or CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> stabilises the hydroperoxide intermediates that can lead to OH formation (Hasson et al., 2005). These findings led to speculation that structurally similar RO<sub>2</sub> may react with HO<sub>2</sub> to produce OH. At that time the only other results to support this contention was a large OH yield  $\alpha=(0.76\pm 0.04)$  from the reaction of HO<sub>2</sub> with CF<sub>3</sub>CF<sub>2</sub>C(O)O<sub>2</sub> (Andersen et al., 2003). Intriguingly, Hasson et al. also suggested that the necessary H-bonding stabilisation could be provided by RO<sub>2</sub> with hydroxyl functionality. This theoretical suggestion has found some support in the experimental observations of Jenkin et al. (2007) who reported a value of  $\alpha_3=(0.20\pm 0.05)$  from the reaction (R3) of HO<sub>2</sub> with the simplest hydroxy peroxy radical, HOCH<sub>2</sub>O<sub>2</sub>:



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Whilst (R1–R3) are atmospherically interesting and worthy of study in their own right, a host of more complex, substituted (carbonyl and/or hydroxyl containing) RO<sub>2</sub> are produced in the atmospheric oxidation of isoprene and other NMHC (Atkinson and Arey, 2003). If significant OH yields were found to be a general feature of HO<sub>2</sub>+ substituted RO<sub>2</sub> reactions, such chemistry would serious impact upon our understanding of atmospheric oxidation. The impact would be particularly large in remote regions, where low anthropogenic activity limits NO<sub>x</sub> levels and suppresses radical propagation via (R4) and (R5):



For example, models predict small [OH] in air over tropical forests, due to rapid losses in reaction with isoprene (R6) and other NMHC, and the lack of verified mechanisms for OH regeneration from the hydroxy-RO<sub>2</sub> produced in (R7).



In a recent Max-Planck-Institute field campaign (GABRIEL), OH was for the first time directly monitored over the Amazonian rainforest. The results (see elsewhere in this issue) clearly demonstrate that large [OH]  $\approx 1 \times 10^7$  molecule cm<sup>-3</sup> were maintained, despite a large (~1 ppb) isoprene loading in otherwise clean air (NO~15 ppt). The largest discrepancies (up to a factor of 10) between measured and modelled [OH] were observed when isoprene mixing ratios were highest, indicating that our understanding of the (low NO<sub>x</sub>) isoprene degradation mechanism is incomplete.

Accordingly, in this work the reactions of HO<sub>2</sub> with a variety of substituted RO<sub>2</sub> were studied, and any OH formed unambiguously identified by a direct OH detection technique. Careful calibration of the experiment allowed the determination of OH product

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yields ( $\alpha$ ) for the reactions of HO<sub>2</sub> with a variety of carbonyl-containing RO<sub>2</sub>, including (R1) and (R2). For experimental reasons (see Sect. 3.4) it was not possible to investigate the RO<sub>2</sub> produced directly from isoprene (R6–R7), however, the reactions of HO<sub>2</sub> with several hydroxy-containing RO<sub>2</sub> were studied, notably (R8) with HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>: and (R9) with CH<sub>3</sub>CH(OH)CH<sub>2</sub>O<sub>2</sub>.



## 2 Experimental

The experiments detailed in this work used Pulsed Laser Photolysis (PLP) generation of HO<sub>2</sub> and RO<sub>2</sub>, coupled to direct, real-time observation of the product OH molecules by pulsed Laser Induced Fluorescence (LIF). Experiments were carried out “back-to-back” with chemical calibrations of the LIF system (see Sect. 2.4), which allowed conversion of fluorescence intensities into absolute [OH], and thus calculation of OH product yields ( $\alpha$ ).

### 2.1 The PLP-LIF technique

The PLP-LIF set-up used in these experiments has recently been used to study a number of OH reactions (Dillon et al., 2005; Dillon et al., 2006a; Dillon et al., 2007; Karunanandan et al., 2007). A detailed description including a schematic diagram of the apparatus was presented previously (Wollenhaupt et al., 2000), so only a brief description is given here. Experiments were conducted in a jacketed quartz reaction cell of volume  $\approx 500 \text{ cm}^3$ . Temperature in the cell was regulated by circulating a cryogenic fluid through the outer jacket, and monitored with a J-Type thermocouple situated close to the intersection of the photolysis and probe laser beams. Pressure was monitored with a 1300 mBar capacitance manometer. Gas flow rates, regulated using calibrated

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mass flow controllers, were between 1000 and 2000 cm<sup>3</sup>(STP) min<sup>-1</sup>. The resulting linear gas velocities in the reaction cell ensured that a fresh gas sample was available for photolysis at each laser pulse (repetition rate 10 Hz), and so prevented a build up of products.

HO<sub>2</sub> and RO<sub>2</sub> radicals were generated from suitable precursors (see Sect. 2.3 below) by the ≈20 ns pulse of an exciplex laser (Lambda Physik, Lextra) operating at 351 nm (XeF). Fluorescence from OH product molecules was excited using the output from a Nd-YAG (Quantel) pumped dye laser (Lambda-Physik, using Rhodamine 6G dye), and detected by a photomultiplier tube shielded by 309 nm (interference) and BG 26 (glass cut-off) filters. Laser excitation spectra of OH (not displayed) with transitions consistent with other recently measured and calculated spectra were used to unambiguously identify OH. All quantitative experiments were conducted at a laser excitation wavelength of λ=281.997 nm, corresponding to the Q<sub>1</sub>(1) line in OH A<sup>2</sup>Σ(v=1)←X<sup>2</sup>Π(v=0). Efficient quenching of the OH fluorescence by the bath gas (air) limited LIF sensitivity, which was measured (see section 2.4) as [OH] ≈5×10<sup>9</sup> molecule cm<sup>-3</sup> for signal:noise=1:1, averaging 10 laser pulses at P=200 mBar.

## 2.2 Reagent handling and concentration measurements

Liquid samples of the following organic reagents were subject to repeated T=77 K freeze-pump-thaw cycles prior to dilution in N<sub>2</sub> and storage in blackened glass bulbs: CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH (both Merck, 99.9%); CH<sub>3</sub>CHO, CH<sub>3</sub>C(O)CH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>CHOH and C<sub>2</sub>H<sub>5</sub>C(O)CH<sub>3</sub> (all Aldrich, 99.5%); C<sub>6</sub>H<sub>5</sub>CHO and (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OH (both Merck, 99%); and isoprene (Aldrich, 99%). NO (Linde) was distilled by repeatedly removing the light boiling fractions at T=77 K, and discarding the frozen residue as the sample was allowed to warm slowly. N<sub>2</sub> and O<sub>2</sub> (Messer 5.0), and Cl<sub>2</sub> (Linde, 2.00% Cl<sub>2</sub> 4.0 in He) were used as supplied.

All reagent concentrations were determined by manometric methods to an estimated accuracy of ±15%, based upon uncertainties in cylinder/bulb partial-pressures, cal-

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ibrated mass flow rates, and absolute measurements of  $T$  and  $P$ . Where possible, online optical determinations of reagent concentration were used as an independent check on the manometric measurements. The simplest optical measurements monitored the absorption at  $\lambda=184.9$  nm in a 43.8 cm long cell, situated downstream of the reaction cell. Briefly, the 184.9 nm line from a low-pressure Hg-lamp was isolated using an interference filter (185 nm, FWHM 10 nm, Oriel), passed through the gas mixture, and the transmitted intensity,  $I$ , recorded on a photodiode. A beam splitter allowed the simultaneous recording (on a reference photodiode) of incident light intensity,  $I_0$ . Literature values (in  $10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>) of  $\sigma_X=6.65$  and 11.8 (Dillon et al., 2005), 22.0 (Salahub and Sandorfy, 1971), and 30.1 (Gierczak et al., 2003) were used to determine concentrations for respectively  $X=\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{CHOH}$  and  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  via the Beer-Lambert relationship, Eq. (1).

$$I = I_0 \exp(-\sigma_X \cdot [X] \cdot l) \quad (1)$$

These optical measurements were found to agree ( $\pm 10\%$ ) with the manometric calculations, and thus verifying the consistency of mass flow controller calibrations etc.

A crucial parameter in all experiments was the concentration of the radical precursor  $\text{Cl}_2$ , which was measured by recording attenuation of ( $220 < \lambda/\text{nm} < 380$  nm) light from a deuterium-lamp in a 30.0 cm cell, inserted serially upstream of the reaction cell. A 0.5 m monochromator (B&M Spektronik BM50, grating 300 lines blazed at 300 nm) collected the light and directed it onto a diode array detector (Oriel INSTAspec 2). Evaluated literature (Atkinson et al., 2007) cross-sections (e.g.  $\sigma_{\text{Cl}_2}=2.55 \times 10^{-19}$  cm<sup>2</sup> at the maximum around 330 nm), were used to obtain  $[\text{Cl}_2]$  (to an estimated accuracy of  $\pm 10\%$ ) from fits of Eq. (1) to the recorded spectra.

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## 2.3 Generation of HO<sub>2</sub> and RO<sub>2</sub>

PLP of Cl<sub>2</sub> (R10) was used to initiate radical chemistry, generating Cl-atoms for conversion into both HO<sub>2</sub> and RO<sub>2</sub>.



5 Laser fluences of around 8 mJ cm<sup>-2</sup> per pulse were used to generate an initial concentration of chlorine atoms, [Cl]<sub>0</sub> ≈ 5 × 10<sup>13</sup> molecule cm<sup>-3</sup>, calculated using a modified version Eq. (2) of the Beer-Lambert law:

$$[\text{Cl}]_0 = 2 \frac{I_0 - I}{l} \quad \text{where } I = I_0 \exp(-\sigma \cdot [\text{Cl}_2] \cdot l) \quad (2)$$

10 where the evaluated literature cross-section of Cl<sub>2</sub> (σ = 1.9 × 10<sup>-19</sup> cm<sup>2</sup> at the photolysis wavelength λ = 351 nm; Atkinson et al., 2007) and photolysis cell length (l = 32 cm) were well-characterised. Under the optically thin conditions prevalent in these experiments, the incident light intensity I<sub>0</sub> (in photons cm<sup>-2</sup>) was obtained from the incident laser fluence, measured using a joulemeter situated behind the photolysis cell. Corrections (20%) were made for the excimer beam divergence, and attenuation by the exit  
15 window. The joulemeter itself had been calibrated in previous work (Dillon et al., 2006b; Dillon et al., 2008). The errors in calculating [Cl]<sub>0</sub> by this method were estimated as ±10% (precision) with an additional ±30% (systematic error/accuracy) associated with imperfections in the photolysis beam profile, and overlap with the probe laser. The presence of large excess CH<sub>3</sub>OH (see below) and O<sub>2</sub> (from the bath gas P > 100 mBar  
20 of air) allowed the rapid conversion (τ < 5 μs) of Cl to HO<sub>2</sub>, and ensured that secondary radical chemistry from (R13) and (R14, α<sub>14</sub> = 0.21) (Atkinson et al., 2007) was minimised:



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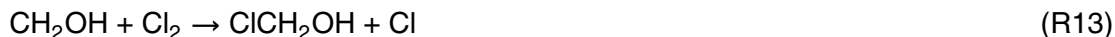
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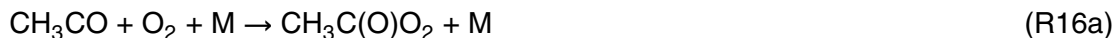
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A small proportion of the Cl-atoms formed in (R10) were sequestered for peroxy radical production. In the study of (R1) for example,  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  was generated by the addition of acetaldehyde,  $\text{CH}_3\text{CHO}$ , to the  $\text{Cl}_2/\text{CH}_3\text{OH}/\text{air}$  mixture:



Typical concentrations (in units of  $10^{14}$  molecule  $\text{cm}^{-3}$ ) of  $[\text{Cl}_2]=80$  to  $100$ ,  $[\text{CH}_3\text{OH}]=40$  to  $180$  and  $[\text{CH}_3\text{CHO}]=2$  to  $12$  were chosen such that Cl was converted to  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  and  $\text{HO}_2$  within  $2 \mu\text{s}$ . The amount of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  present in each experiment was controlled by the (well-characterised) relative rates of (R11) and (R15), and for the purposes of experimental planning/design could be estimated from Eq. (3):

$$10 \quad [\text{CH}_3\text{C}(\text{O})\text{O}_2] \approx [\text{Cl}]_0 \frac{k_{15} [\text{CH}_3\text{CHO}] \cdot (1 - \alpha_{16})}{k_{15} [\text{CH}_3\text{CHO}] + k_{11} [\text{CH}_3\text{OH}]} \quad (3)$$

where the term  $(1 - \alpha_{16})$  is close to unity in these experiments as OH production in (R16b) is efficient only at low pressures ( $\alpha_{16} < 0.1$  at all experimental  $P > 100$  mBar used here (Carr et al., 2007)). In practice the majority (>80%) of

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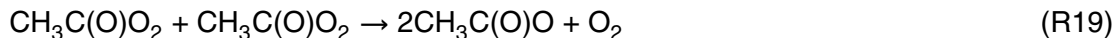
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the Cl produced in (R10) was used to generate HO<sub>2</sub>. The resulting conditions of [HO<sub>2</sub>] > [RO<sub>2</sub>], together with the slow and radical-terminating self-reaction (R18) of HO<sub>2</sub> ( $k_{18} < 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at all experimental  $P < 1$  Bar used here) simplified data analysis and minimised unwanted radical generation in the fast, radical propagating (R19) ( $k_{19} = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; Atkinson et al., 2007).



## 2.4 Calibration of the OH LIF detection system

LIF is a direct, but non-absolute technique, which meant that the detection system required calibration prior to conversion of OH fluorescence signals into absolute concentrations. A suitable calibration reaction was (R4), (HO<sub>2</sub>+NO), as the yield of OH is known to be close to unity ( $\alpha_4 = 0.984$ ), and conveniently the rate coefficient ( $k_4 = 8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; Atkinson et al., 2007) is similar to the rate coefficients for a number of HO<sub>2</sub>+RO<sub>2</sub> reactions (e.g.  $k_1 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Accordingly, small flows of NO were added to the Cl<sub>2</sub>/CH<sub>3</sub>OH/air photolysis mixture to generate well-characterised amounts of OH in conditions of  $P$ , [Cl<sub>2</sub>], [CH<sub>3</sub>OH], etc. as close as possible to those in the experiments to investigate (R1), i.e. with [HO<sub>2</sub>] > [NO] ( $\approx [\text{CH}_3\text{C}(\text{O})\text{O}_2]$ ).

Figure 1 displays the results of a series of calibration experiments, where three different measured [NO] ( $97, 83$  and  $47 \times 10^{11} \text{ molecule cm}^{-3}$ ) were converted (R4) to OH by an excess [HO<sub>2</sub>] =  $6.4 \times 10^{13} \text{ molecule cm}^{-3}$ . Calibration was achieved via numerical simulation of the data using the FACSIMILE program (Curtis and Sweetenham, 1987). Experimentally determined values of  $P$ , [Cl<sub>2</sub>], [CH<sub>3</sub>OH], [NO] and the laser fluence were used to initiate simulations, from which output values of [OH] were generated using the list of reactions and literature rate coefficients given in Appendix A. The relative position of the (arbitrary) LIF to the (absolute) [OH] y-axes was determined by scaling

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the OH LIF signals to their corresponding simulations. Calibration experiments were conducted prior to, between and after experiments to investigate (R1). The duration of a typical series of three calibrations interrupted by two experiments to determine  $\alpha_1$ , was about 40 min, in which time fluctuations in LIF sensitivity were rarely significant.

5 The shapes of the OH profiles presented in Fig. 1 are initially counter-intuitive. Whilst OH is generated on the millisecond timescale of (R4), rapid loss processes, dominated by reactions (R20–21) with CH<sub>3</sub>OH and HO<sub>2</sub>, prevent [OH] from reaching its theoretical maximum value, which is equivalent to the parent [NO].



For example, in Fig. 1 the open circle datapoints correspond to OH formed (R4) from [NO]= $8.3 \times 10^{12}$  molecule cm<sup>-3</sup> at an approximate first-order rate  $k_4[\text{HO}_2] \approx 500 \text{ s}^{-1}$ . OH is efficiently removed ( $k_{20}[\text{CH}_3\text{OH}] + k_{21}[\text{HO}_2] \approx 10\,000 \text{ s}^{-1}$ ) before (R4) is complete, limiting the observed [OH] to a maximum value of  $\approx 3 \times 10^{11}$  molecule cm<sup>-3</sup>. Note that all  
15 simulations adequately reproduced the shape of the OH decay profiles, which was controlled by the slower first-order rate of (R4),  $k_4[\text{HO}_2]$ . Since  $k_4$  itself is well-known (Atkinson et al., 2007), it follows that calibration experiments such as those presented in Fig. 1 provide an independent validation of the values of  $[\text{HO}_2] \approx [\text{Cl}] - [\text{CH}_3\text{C}(\text{O})\text{O}_2]$  calculated from Eqs. (2–3).

20 Potential systematic errors in the calibration process included interference from other fluorescing species, unwanted secondary OH production, and uncertainties in both (experimentally determined) reagent concentrations and the (literature) photochemical parameters used to simulate  $[\text{OH}]_t$ . Accordingly, experiments were conducted in which the probe laser was tuned away from the OH line (to  $\lambda=282.01 \text{ nm}$ ), whereupon no  
25 fluorescence was detected, indicating that OH and only OH contributed to the calibration profiles. Sensitivity analysis demonstrated that known secondary OH production, e.g. from (R14b) ( $\text{HO}_2 + \text{Cl} \rightarrow \text{OH} + \text{ClO}$ ) was a negligible source of error. As is evident

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from the data recorded in the absence of NO (see Fig. 1, open triangle datapoints), LIF signals from (R14b) were small, and were removed within 300  $\mu\text{s}$  (i.e. occurred on a completely different timescale to R4), and were anyway adequately accounted for in the simulations. As a result we consider the overall accuracy of the calibrations to be limited by uncertainties in reactant concentrations, particularly of NO ( $\pm 15\%$ ), and the evaluated error in the most important rate parameter  $k_4$ , ( $\pm 26\%$ ; Atkinson et al., 2007) which when combined (in a squared sum) give an estimate for the overall uncertainty of  $\pm 30\%$  for the calibration process.

### 3 Results and discussion

The experiments detailed in this work were conducted under conditions of  $[\text{HO}_2] > [\text{RO}_2] \approx [\text{NO}]$ , and as a result unwanted secondary radical generation was minimised. Nonetheless, the reaction mixtures were chemically quite complex, containing several radical species, including more than one potential source of OH. Analysis by conventional least-squares fitting techniques was therefore not applicable, and all results were obtained following numerical simulation of the data using the FACSIMILE program (Curtis and Sweetenham, 1987). Typically, experimental values of the laser fluence,  $P$ ,  $[\text{Cl}_2]$ ,  $[\text{CH}_3\text{OH}]$ , and concentration of  $\text{RO}_2$  precursor e.g.  $[\text{CH}_3\text{CHO}]$  were used to initiate the simulations. Output values of  $t$ ,  $[\text{Cl}]$ ,  $[\text{HO}_2]$ ,  $[\text{RO}_2]$ , and  $[\text{OH}]$  were generated using the list of reactions and literature rate coefficients given in Appendix A.

3.1  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow \text{OH} + \text{other products}$ , (R1)

3.1.1 Determination of OH yield  $\alpha_1$

Figure 2 displays the results of a typical experiment, conducted at  $T = 298\text{ K}$  and  $P = 229\text{ mBar}$ , to determine the yield  $\alpha_1$  of OH, formed in  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$  (R1). The

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LIF signals were calibrated as described in Sect. 2.4. For clarity, only one calibration dataset (open black circles in Fig. 2 [ $\text{NO}] = 8.3 \times 10^{12}$  molecule  $\text{cm}^{-3}$ ) is displayed here. The blue square datapoints show the LIF signal recorded following generation of [ $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ] =  $7.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$  in the presence of [ $\text{HO}_2$ ] =  $5.4 \times 10^{13}$  molecule  $\text{cm}^{-3}$ . The LIF signal is of a comparable size to (factor of  $\approx 2$  smaller) and decays on a similar timescale to the calibration signal. In experiments where the probe laser was tuned away from the OH line (e.g. green triangle datapoints in Fig. 2 where  $\lambda = 282.01$  nm), no fluorescence was detected. These observations indicate that OH is indeed formed at significant yield from (R1).

More quantitative results were obtained by numerical simulation of the experiment. The solid red line that passes through the datapoints on Fig. 2 indicates the result of simulating the [ $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ] =  $7.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$  (blue squares) experiment using  $\alpha_1 = 0.5$  and the recommended literature rate coefficient of  $k_1 = 1.4 \times 10^{-11}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  (Atkinson et al., 2007). The simulation reproduced the experiment well, and was particularly sensitive to  $\alpha_1$ , as is demonstrated in Fig. 2 where simulations (red dotted-lines) using  $\alpha_1 = 0.4$  and  $\alpha_1 = 0.6$  are also displayed. The overall accuracy of our determination of  $\alpha_1$  was however governed by systematic uncertainties associated with the LIF calibration, and parameters used in the simulations. Errors associated with secondary radical production, including other known sources of OH, were assessed, but found to be insignificant. Figure 3 displays the full output of the same simulation, including profiles of [ $\text{HO}_2$ ], [ $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ], [ $\text{OH}$ ] and other products of (R1), on logarithmic scale. The simulation shows that a large excess of  $\text{HO}_2$  was maintained throughout the experiment, ensuring that (R1) was the principal fate for  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ . Both (R14b) ( $\text{Cl} + \text{HO}_2$ ) and (R16b) ( $\text{CH}_3\text{CO} + \text{O}_2$ ) were known to be minor secondary sources of OH in these experiments. Nonetheless, as was shown by the open triangles data in Fig. 1, the maximum ( $[\text{CH}_3\text{CHO}] = 0$ ) impact of (R14b) was small. The contributions of (R14b) and (R16b) were assessed individually by simulation, as presented in Fig. 3. Both reactions occur on a much shorter timescale than (R1), and because of the short chemical lifetime of OH in these experiments, their contribution to

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the overall [OH] observed was negligible after about 100  $\mu$ s.

Table 1 lists the conditions and results of all experiments to study (R1). A set of experiments (corresponding to one row in Table 1) generally consisted of determinations of  $\alpha_1$  from two or more different [CH<sub>3</sub>C(O)O<sub>2</sub>], generated by changing the parent CH<sub>3</sub>CHO concentration. Conditions of  $P$ ,  $T$  and reagent concentrations were otherwise unchanged. Note that values of [HO<sub>2</sub>] were not listed explicitly as these changed slightly from the calibration (where [HO<sub>2</sub>]  $\approx$  [Cl]<sub>0</sub>) to the (R1) experiments (where [HO<sub>2</sub>]  $\approx$  [Cl]<sub>0</sub> - [CH<sub>3</sub>C(O)O<sub>2</sub>]). New calibration data was required for experiments conducted at different  $P$ , as the LIF detection sensitivity was strongly influenced by fluorescence quenching by the bath gas (air). There was no systematic change in the  $\alpha_1 \approx 0.5$  required to simulate experimental observations, which were obtained over a range pressures (100–705 mBar) and at around ambient  $T$ . The range of precursor concentrations was necessarily limited so as to minimise secondary chemistry e.g. in (R13–14), (R16b–17) and (R18–R19), whilst maintaining a suitable millisecond timescale for (R1). The uncertainties in  $\alpha_1$  quoted in Table 1 refer to the internal consistency of the calibration and  $\alpha_1$  data (i.e. data from Fig. 2 listed as  $\alpha_1 = (0.5 \pm 0.05)$  as we can distinguish it from  $\alpha_1 = 0.4$  or 0.6).

A weighted average (using these precision-only errors) of the data in Table 1 gives  $\alpha_1 = (0.52 \pm 0.02)$ . A more realistic assessment of the overall uncertainty in  $\alpha_1$  was obtained by combining this statistical error with the LIF calibration uncertainty ( $\pm 30\%$ , see Sect. 2.4), and errors associated with the simulations of (R1). Note that since these experiments were conducted back-to-back with the LIF calibrations, errors associated with a number of important parameters (e.g. [HO<sub>2</sub>], OH lifetime,  $P$ ,  $T$ ) cancelled-out, and could be neglected when assessing the overall uncertainty in  $\alpha_1$ . Sensitivity analysis identified the remaining critical parameters as those controlling the concentration of parent radicals, [CH<sub>3</sub>C(O)O<sub>2</sub>], and the rate coefficient for conversion to OH,  $k_1$ . Uncertainties in: laser fluence ( $\pm 20\%$ ); [Cl<sub>2</sub>] ( $\pm 10\%$ ); relative [CH<sub>3</sub>CHO] to [CH<sub>3</sub>OH] ( $\pm 10\%$ ); rate coefficients  $k_{15}$  and  $k_{12}$  (relative rate measured both relative to C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> to about  $\pm 5\%$ ; Tyndall et al., 1999) were therefore combined to give an overall estimate

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of  $\pm 25\%$  in  $[\text{CH}_3\text{C}(\text{O})\text{O}_2]$ . This value was combined with an effective uncertainty in  $k_1$  ( $\pm 15\%$ , see Sec. 3.1.2 below) and that of the LIF calibration process ( $\pm 30\%$ ), to obtain an overall estimated accuracy of 40%, or  $\alpha_1 = (0.5 \pm 0.2)$ .

### 3.1.2 Determination of the rate coefficient $k_1$ , and uncertainties therein

5 All values of  $\alpha_1$  listed in Table 1 were obtained from simulations using the evaluated literature rate coefficient  $k_1(298\text{ K}) = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which was based upon the results of two laboratory studies (Moortgat et al., 1989; Tomas et al., 2001). A large uncertainty of approximately a factor of two is quoted (Atkinson et al., 2007) to account for possible systematic errors. LIF detection of OH, used to monitor (R1)  
10 in this work, allowed for a more precise value of  $k_1(298\text{ K})$  to be determined, as many of the problems associated with earlier studies were avoided. Firstly, LIF is a more selective technique than the monitoring of overlapping UV absorptions from  $\text{HO}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , used in the earlier kinetic studies (Moortgat et al., 1989; Tomas et al., 2001). Second, LIF is also more sensitive than conventional absorption techniques,  
15 allowing smaller radical concentrations to be used. As a result, the experiments could be conducted under kinetic conditions which minimised unwanted radical losses (see below).

With reference to Fig. 3, retrieval of  $k_1$  was aided by having one reagent ( $\text{HO}_2$ , orange dotted line) in large excess over the course of the experiment. As a result the  
20 kinetic profile was (to a first approximation) governed by  $[\text{HO}_2]$  and  $k_1$ . OH has a very different time profile to the other products of (R1), and in effect acts as a “spectroscopic marker” for its parent radical  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  (green dot-dashed line). Simulations which used  $k_1$  values at the upper or lower limits of the recommendation ( $2.8 \times 10^{-11}$  and  $7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) were not consistent with any data recorded in this work.  
25 Simulations using  $(1.1 < k_1 < 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were able to reproduce the data (whilst adjusting  $\alpha_1 \pm 20\%$ ) within the noise. It was this uncertainty of  $\pm 20\%$  in  $k_1$  which propagates into the overall error in  $\alpha_1$ , as systematic errors in  $[\text{HO}_2]$  were also

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present in the back-to-back calibrations (R4) experiments.

Secondary radical processes, which occurred in the earlier studies (Moortgat et al., 1989; Tomas et al., 2001), were of little consequence here. Sensitivity analysis demonstrated that the  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  self-reaction (R19) accounted for less than 12% of the  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  loss rate under all conditions. Inclusion of the equilibrium process (R22) had no discernable impact on the simulations as relatively small  $[\text{CH}_3\text{CHO}] < 1 \times 10^{15}$  molecule  $\text{cm}^{-3}$  were used in this work.



That OH was not then recognised as a significant product of (R1) introduces the largest uncertainty into earlier  $k_1$  determinations (Atkinson et al., 2007). Recycling of reactants via the reactions of OH with  $\text{CH}_3\text{OH}$  (R20) and  $\text{CH}_3\text{CHO}$  (R23), was not accounted for in previous analyses (Moortgat et al., 1989; Tomas et al., 2001), as no production of OH in (R1) was anticipated.



In this work regeneration of  $\text{HO}_2$  was of no consequence, as this reagent was in excess, whilst regeneration of  $\text{CH}_3\text{CO}$  in (R23) was kept to a minimum (in all experiments <20%) by the use of small  $[\text{CH}_3\text{CHO}]$ .

We conclude that, whilst these experiments were designed primarily to determine  $\alpha_1$ , the high selectivity and sensitivity of the OH LIF detection technique has allowed the uncertainties in  $k_1(298\text{K})$  to be reduced. The principal source of error in these determinations was the  $\pm 30\%$  uncertainty in  $[\text{HO}_2]$ , which when added to statistical errors results in an absolute value of  $k_1(298\text{K}) = (1.4 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We note that uncertainties in this parameter could be further reduced if the excess reagent  $\text{HO}_2$  was monitored, in addition to OH.

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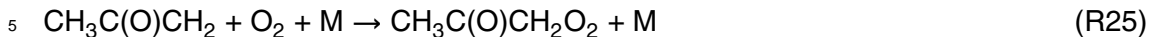
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## 3.2 HO<sub>2</sub>+CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>→ products (R2)

Photolysis (R10) of Cl<sub>2</sub> in the presence of acetone, CH<sub>3</sub>C(O)CH<sub>3</sub>, was used to generate acetyl peroxy radicals for the investigation of (R2) (HO<sub>2</sub>+CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>).



Similar methods to those detailed above were used to simultaneously generate an excess of HO<sub>2</sub> (R11–12), see Sect. 2.3, and to calibrate the OH LIF signals (see Sect. 2.4). The black diamonds datapoints in Fig. 4 represent the [OH]<sub>t</sub> obtained at *P*=230 mBar from [CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>]=5.2×10<sup>12</sup> molecule cm<sup>-3</sup> in the presence of [HO<sub>2</sub>]=5.8×10<sup>13</sup> molecule cm<sup>-3</sup>. It was apparent from this and similar datasets (see Table 2 for details) that the yield of OH from (R2) was considerably smaller than the only literature value (Hasson et al., 2004) of α<sub>2</sub>=(0.67±0.20). Numerical simulation of the data using the list of reactions in Appendix A, and α<sub>2</sub>=0.7 generated [OH]<sub>t</sub> profiles (e.g. red-dotted line in Fig. 4) that grossly overestimated every experimental observation. A significant α<sub>2</sub>>0 was nonetheless required to adequately simulate the data, with α<sub>2</sub>≈0.15 (e.g. the dot-dashed line in Fig. 4) giving best results.

Such a large discrepancy between the results of this work, and those obtained by Hasson et al. was a source of concern. As a check on the reliability and reproducibility of the PLP/calibrated-LIF method used in this work, back-to-back experiments were conducted where CH<sub>3</sub>C(O)CH<sub>3</sub> was replaced by a kinetically equivalent amount of CH<sub>3</sub>CHO (i.e. *k*<sub>15</sub>[CH<sub>3</sub>CHO]≈*k*<sub>24</sub>[CH<sub>3</sub>C(O)CH<sub>3</sub>]). The OH produced in (R2) and (R1) could then be compared directly. Such relative yield experiments do not rely exclusively upon LIF calibration in (R4), and as such were useful as a double-check on laser alignment etc. The blue square datapoints in Fig. 4 display the resulting OH profile from (R1), which indicates that α<sub>1</sub>*gg*α<sub>2</sub>, again in contrast to the literature results (Hasson et al., 2004).

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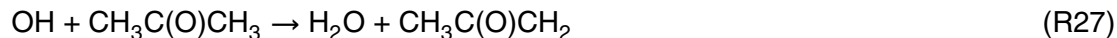
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One difference between the (R2) and (R1) experiments was the use of considerably larger  $[\text{CH}_3\text{C}(\text{O})\text{CH}_3]$  ( $\sim 10^{16}$  molecule  $\text{cm}^{-3}$ , see Table 2) than  $[\text{CH}_3\text{CHO}]$  ( $< 10^{15}$  molecule  $\text{cm}^{-3}$ ) to generate similar concentrations of  $\text{RO}_2$ . This was an unavoidable result of differences in reactivity towards Cl (in  $10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ :  $k_{24}=2.1$  whereas  $k_{15}=80$ ). Changes in LIF sensitivity due to physical quenching were not anticipated, as in these experiments  $\text{O}_2$  (20% of the bath gas), was always present in large excess, and is an efficient quencher of OH ( $k_{\text{O}}=1.4 \times 10^{-10}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ ; Bailey et al., 1997). Nonetheless, it was thought prudent to directly monitor the OH LIF response to the presence of such large  $[\text{CH}_3\text{C}(\text{O})\text{CH}_3]$  in experiments using  $\text{H}_2\text{O}_2$  photolysis (R26) as a direct, well-characterised source of OH.



No  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  mediated quenching of the OH LIF signals was observed. In the course of these experiments, the rate coefficient  $k_{27}=(1.9 \pm 0.2) \times 10^{-13}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  was obtained, in good agreement with the evaluated literature ( $k_{27}=(1.8 \pm 0.4) \times 10^{-13}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ ; Atkinson et al., 2007) thereby increasing confidence in the supply of acetone, and the (R2) reaction system.

It was difficult to obtain more information about (R2), as the only species detected (OH) was produced at such small yield. Simulations were generally initiated using the evaluated literature value of  $k_2(298 \text{ K})=9.0 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$ . This recommendation is based on the results of just one experimental study (Bridier et al., 1993), and is consequently quoted with an uncertainty of approximately a factor of 2. An improved reproduction of the data was achieved (e.g. in Fig. 4) when values close to the lower error limit for  $k_2$  of  $5 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$   $\text{s}^{-1}$  were used. However, given that OH is produced via (R1) which follows the break-up (R28) of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$  and rapid conversion (R16) of  $\text{CH}_3\text{CO}$  to  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ , Bridier et al. should have underestimated

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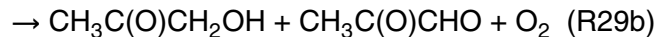
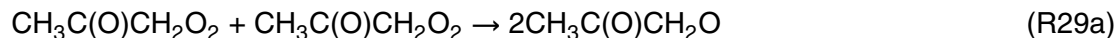
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$k_2$ .



Secondary OH production in this reaction system is, however quite difficult to quantify, as losses of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  include (R29) which also produces  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$  and ultimately OH.



Approximately equal amounts of  $\text{HO}_2$  and  $\text{RO}_2$  were used in the earlier kinetic study (Bridier et al., 1993), leading to near 50% of initial  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  reacting via (R29) rather than (R2). Similarly, in the experiments of Hasson et al. a significant proportion (>30%) of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  was lost in (R29). Subsequent OH formation from the reaction sequence (R29a), (R28), and (R1) was included in their analysis (Hasson et al., 2004), though it is unclear how sensitive their result of  $\alpha_2=(0.67\pm 0.2)$  is to the values of  $k_2$  and  $k_{29}$  used. Note that due to the experimental conditions of  $[\text{HO}_2]>[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2]$  used in this work, (R2) accounted for >90% of  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  loss. Secondary OH production via (R29a), (R28), (R16) and (R1) was therefore minimised. We are confident therefore in the result of  $\alpha_2=(0.15\pm 0.10)$  obtained in this work, but note that inconsistencies remain in the values of  $k_2$  used here and those of Bridier et al. Further experiments in which  $\text{HO}_2$ ,  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$  and OH were monitored would help to resolve these issues.

### 3.3 The reaction (R8) $\text{HO}_2+\text{HOCH}_2\text{CH}_2\text{O}_2\rightarrow$ (products)

Photolysis (R10) of  $\text{Cl}_2$  in the presence of ethanol was used to generate a simple hydroxyperoxy radical,  $\text{HOCH}_2\text{CH}_2\text{O}_2$ , and  $\text{HO}_2$ :

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Conveniently, the reaction sequence (R30–32) produced the large excess of  $[\text{HO}_2] > [\text{HOCH}_2\text{CH}_2\text{O}_2]$  required to determine  $\alpha_8$ . As a result these experiments were conducted in the absence of  $\text{CH}_3\text{OH}$ . Figure 5 displays the results of one such experiment conducted at  $T=298\text{ K}$  and  $P=250\text{ mBar}$ . The open black circles describe data where  $[\text{NO}] = 2.9 \times 10^{12}\text{ molecule cm}^{-3}$  was used to generate (R4) a known amount of OH and hence calibrate the LIF detection system. The red stars show the comparatively small amount of OH generated from  $[\text{HOCH}_2\text{CH}_2\text{O}_2] = 5.3 \times 10^{12}\text{ molecule cm}^{-3}$  in the presence of  $[\text{HO}_2] = 5.6 \times 10^{13}\text{ molecule cm}^{-3}$ . Numerical simulation using the recommended  $k_8 = 1.2 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Atkinson et al., 2007), demonstrated that small OH yields of  $\alpha_8 \approx 0.02$  were required to reproduce this and similar datasets (see Table 2). To account for uncertainties particularly in  $k_8$  ( $\pm 60\%$ ) we quote a conservative upper-limit of  $\alpha_8 < 0.04$ . Similar results were obtained at  $T=257$  and  $351\text{ K}$ .

### 3.4 OH yields for other $\text{HO}_2 + \text{RO}_2$ reactions

The methods detailed in section 2 were used to measure OH product yields for the reactions of a number of other substituted peroxy radicals with  $\text{HO}_2$ . Common to each system studied was PLP generation (R10) of  $[\text{Cl}] = 7 \times 10^{13}\text{ molecule cm}^{-3}$ , in the presence of  $[\text{CH}_3\text{OH}] = 6 \times 10^{15}\text{ molecule cm}^{-3}$  and  $P=220\text{ mBar}$  (air) to facilitate formation (R11–12) of the excess reagent  $\text{HO}_2$ . The OH LIF system was calibrated using  $\text{HO}_2 + \text{NO}$  (R4), as described in Sect. 2.4. Note that simulation of the observed OH profiles relied upon a host of kinetic data (see Appendix A), which was not completely

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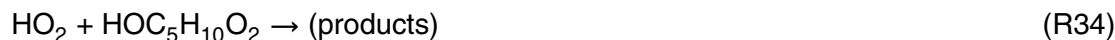
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available. Crucially, no literature rate coefficients for the  $\text{HO}_2 + \text{RO}_2$  reactions were found, therefore an estimated value of  $k = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was adopted for all such processes. As a result, the values of  $\alpha$  listed in Table 2 (excepting  $\alpha_2$  and  $\alpha_8$ ) should be regarded as no more than semi-quantitative.

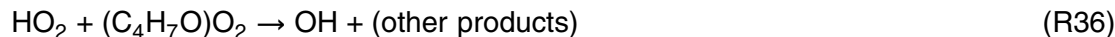
5 No evidence for OH production was observed upon addition of  $(\text{CH}_3)_2\text{CHOH}$  to the  $\text{Cl}_2/\text{CH}_3\text{OH}/\text{air}$  photolysis mixture for the study of (R9) ( $\text{HO}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2$ ). Following consideration of the noise on the LIF signals, and uncertainties in the estimated value of  $k_9 = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used, a conservative upper-limit of  $\alpha_9 < 0.06$  was assigned. It was unfortunately not possible to investigate  $\text{RO}_2$  generated from  
10 unsaturated precursors, such as the atmospherically important hydroxyperoxy radicals produced (R6–7) from isoprene. Addition of isoprene to the  $\text{Cl}_2/\text{CH}_3\text{OH}/\text{air}$  photolysis mixture produced a mixture of  $\text{C}_5\text{H}_8\text{ClO}_2$  isomers in an excess of  $\text{HO}_2$ , from which no OH was observed ( $\alpha_{33} < 0.03$ , see Table 2).



15 Addition of isopentanol to the photolysis mixture was used to generate structurally similar (saturated) analogues of the target isoprene hydroxyperoxys. No OH production was observed however, and an upper-limit of  $\alpha_{34} < 0.06$  was derived.



By contrast, strong evidence for OH formation was observed ( $\alpha \approx 0.2$ ) for the reac-  
20 tions of  $\text{HO}_2$  with  $\text{RO}_2$  containing a carbonyl group, e.g. those from benzaldehyde and butanone:



## 4 Atmospheric implications and conclusions

OH was, for the first time, directly observed as a product from reactions of HO<sub>2</sub> with peroxy radicals. For the reaction (R1) (HO<sub>2</sub>+CH<sub>3</sub>C(O)O<sub>2</sub>), an OH product yield  $\alpha_1=(0.5\pm 0.2)$  was measured, in good agreement with two recent indirect determinations (Hasson et al., 2004; Jenkin et al., 2007). The rate coefficient  $k_1(298\text{ K})=(1.4\pm 0.5)\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ , was determined, substantially reducing the uncertainties in this important atmospheric parameter. OH products were also observed from the reactions of HO<sub>2</sub> with three other carbonyl-containing RO<sub>2</sub> (produced from acetone, benzaldehyde and butanone). These results imply that a host of HO<sub>2</sub>+carbonyl-RO<sub>2</sub> reactions, previously considered to be radical-terminating, may produce OH in the atmosphere. For (R2) (HO<sub>2</sub>+CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>) the measured  $\alpha_2\approx 0.15$  was considerably smaller than in the only literature determination (Hasson et al., 2004). By contrast OH was not observed as a major product from reactions where carbonyl functionality was absent, e.g. the reactions of HO<sub>2</sub> with hydroxy-containing RO<sub>2</sub>. Conservative upper-limits were assigned for the reactions of HO<sub>2</sub> with HOCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub> (R8,  $\alpha_8 < 0.04$ ), CH<sub>3</sub>CH(OH)CH<sub>2</sub>O<sub>2</sub> (R9,  $\alpha_9 < 0.06$ ) and HOC<sub>5</sub>H<sub>10</sub>O<sub>2</sub> (R34,  $\alpha_{34} < 0.06$ ).

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## Appendix A

### List of reactions and rate parameters used in data simulations

(R11)	$\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}$	$5.5 \times 10^{-11}$	
(R14a)	$\text{Cl} + \text{HO}_2 \rightarrow$	$(1 - 1.7 \exp(-620 / T)) \times 4.4 \times 10^{-11}$	
(R14b)	$\text{Cl} + \text{HO}_2 \rightarrow \text{OH} + \text{ClO}$	$1.7 \exp(-620 / T) \times 4.4 \times 10^{-11}$	
(R12)	$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO}$	$9.7 \times 10^{-12}$	
	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO}$	$7.4 \times 10^{-14} \exp(-1080 / T)$	
(R13)	$\text{CH}_2\text{OH} + \text{Cl}_2 \rightarrow \text{Cl}$	$2.9 \times 10^{-11}$	(Tyndall et al., 1999)
(R4)	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$3.6 \times 10^{-12} \exp(270 / T)$	
(R18)	$\text{HO}_2 + \text{HO}_2 \rightarrow$	$2.2 \times 10^{-13} \exp(600 / T) + 1.9 \times 10^{-33} [\text{M}] \exp(980 / T)$	
(R20a)	$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}$	$0.85 \times 6.38 \times 10^{-5} T^2 \exp(144 / T)$	
(R20b)	$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}$	$0.15 \times 6.38 \times 10^{-5} T^2 \exp(144 / T)$	
(R21)	$\text{OH} + \text{HO}_2 \rightarrow$	$4.8 \times 10^{-11} \exp(250 / T)$	
	$\text{OH} + \text{NO} + \text{M} \rightarrow$	$k_0 = 7.4 \times 10^{-31} [\text{N}_2], k_\infty = 3.3 \times 10^{-11}, \text{Fc} = 0.81$	
	$\text{ClO} + \text{NO} \rightarrow \text{Cl}$	$6.2 \times 10^{-12} \exp(295 / T)$	
	$\text{ClO} + \text{HO}_2 \rightarrow$	$2.2 \times 10^{-12} \exp(340 / T)$	

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(R15)	$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO}$	$8.0 \times 10^{-11}$	
(R16a)	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2$	$(1 - \alpha_{16}) \times 5.1 \times 10^{-12}$	
(R16b)	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{OH}$	$\alpha_{16} \times 5.1 \times 10^{-12}$	
(R17)	$\text{CH}_3\text{CO} + \text{Cl}_2 \rightarrow \text{Cl}$	$4.3 \times 10^{-11}$	(Tyndall et al., 1999)
(R22)	$\text{HO}_2 + \text{CH}_3\text{CHO} \leftrightarrow \text{CH}_3\text{C}(\text{OH})\text{O}_2$	$k_{22} = 4.4 \times 10^{-14}$ , $K_{22} = 1.9 \times 10^{-27} \exp(6925 / T)$ $\text{cm}^3 \text{ molecule}^{-1}$ .	(Tomas et al., 2001)
(R23)	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO}$	$4.4 \times 10^{-12} \exp(365 / T)$	
(R1c)	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{OH} + \text{CH}_3$	$k_1 \times \alpha_1$	(varied, this work)
(R1ab)	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow$	$k_1 \times (1 - \alpha_1)$	(varied, this work)
(R19)	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow 2\text{CH}_3$	$2.9 \times 10^{-12} \exp(500 / T)$	
(R2a)	$\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow \text{OH} + \text{CH}_3\text{CO}$	$(1 - \alpha) \times k_2$	(varied, this work)
(R2b)	$\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow \text{OH} + \text{CH}_3\text{CO}$	$\alpha \times k_2$ (varied, this work)	
(R24)	$\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2$	$2.1 \times 10^{-12}$	
(R27)	$\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2$	$1.8 \times 10^{-13}$	
(R25)	$\text{CH}_3\text{C}(\text{O})\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$	$1 \times 10^{-12}$	
	$\text{CH}_3\text{C}(\text{O})\text{CH}_2 + \text{Cl}_2 \rightarrow \text{Cl}$	$4.3 \times 10^{-11}$ (estimate)	
(R29a)	$2\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow 2\text{CH}_3\text{CO}$	$0.63 \times 8 \times 10^{-12}$	
(R29b)	$2\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow$	$0.37 \times 8 \times 10^{-12}$	
(R8a)	$\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow$	$(1 - \alpha_8) \times 1.4 \times 10^{-11}$	(varied, this work)
(R8b)	$\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow \text{OH} + \text{O}_2 + \text{HOCH}_2\text{CH}_2\text{O}$	$\alpha_8 \times 1.4 \times 10^{-11}$	(varied, this work)
(R30a)	$\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH} + \text{HCl}$	$0.92 \times 8.6 \times 10^{-11}$	
(R30b)	$\text{Cl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH}_2\text{OH}$	$0.08 \times 8.6 \times 10^{-11}$	
(R31)	$\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_3\text{CHO}$	$1.9 \times 10^{-11}$	

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(R32)	$\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 + \text{M} \rightarrow \text{HOCH}_2\text{CH}_2\text{O}_2 + \text{M}$	$3.0 \times 10^{-12}$	
	$\text{CH}_3\text{CHOH} + \text{Cl}_2 \rightarrow \text{Cl}$	$3 \times 10^{-11}$ (estimate)	
	$\text{CH}_2\text{CH}_2\text{OH} + \text{Cl}_2 \rightarrow \text{Cl}$	$3 \times 10^{-11}$ (estimate)	
	$\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHOH}$	$3.0 \times 10^{-12} \times \exp(20 / T)$	
	$2\text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow$	$0.5 \times 7.8 \times 10^{-14} \times \exp(1000 / T)$	
	$2\text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow 2\text{HOCH}_2\text{CH}_2\text{O}$	$0.5 \times 7.8 \times 10^{-14} \times \exp(1000 / T)$	
(R9a)	$\text{HO}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2 \rightarrow$	$(1 - \alpha_9) * 1 \times 10^{-11}$	(estimate, this work)
(R9b)	$\text{HO}_2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{O}_2 \rightarrow \text{OH}$	$\alpha_9 * 1 \times 10^{-11}$	(estimate, this work)
	$\text{Cl} + (\text{CH}_3)_2\text{CHOH} \rightarrow (\text{CH}_3)_2\text{COH}$	$0.85 \times 8.6 \times 10^{-11}$	(Yamanaka et al., 2007)
	$\text{Cl} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_2$	$0.15 \times 8.6 \times 10^{-11}$	(Yamanaka et al., 2007)
	$(\text{CH}_3)_2\text{COH} + \text{O}_2 \rightarrow \text{HO}_2$	$1.9 \times 10^{-11}$	
	$\text{CH}_3\text{C}(\text{OH})\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{O}_2$	$1 \times 10^{-11}$	(estimate)
	$\text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{O}_2 + \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{O}_2 \rightarrow$	$2 \times 10^{-12}$	(estimate)
	$\text{OH} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_2$	$5.1 \times 10^{-12}$	
(R33-36)	$\text{HO}_2 + \text{RO}_2 \rightarrow$	$(1 - \alpha) \times 1 \times 10^{-11}$	(estimate, this work)
(R33-36)	$\text{HO}_2 + \text{RO}_2 \rightarrow \text{OH}$	$\alpha \times 1 \times 10^{-11}$	(estimate, this work)
	$\text{Cl} + \text{C}_8\text{H}_8 \rightarrow \text{R}$	$3.4 \times 10^{-10}$	(Bedjanian et al., 1998)
	$\text{OH} + \text{C}_8\text{H}_8 \rightarrow \text{R}$	$1.0 \times 10^{-10}$	
	$\text{Cl} + (\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{OH} \rightarrow \text{R}$	$0.5 \times 2.5 \times 10^{-10}$	(estimate, (Wu et al., 2003))
	$\text{Cl} + (\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{OH} \rightarrow \text{HO}_2$	$0.5 \times 2.5 \times 10^{-10}$	(estimate, (Wu et al., 2003))
	$\text{OH} + (\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{OH} \rightarrow \text{R}$	$1.4 \times 10^{-11}$	(Wu et al., 2003)

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$\text{Cl} + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{R}$	$9.6 \times 10^{-11}$	(Noziere et al., 1994)
$\text{OH} + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{R}$	$1.3 \times 10^{-11}$	(Baulch et al., 1994)
$\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 \rightarrow \text{R}$	$3.6 \times 10^{-11}$	
$\text{OH} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 \rightarrow \text{R}$	$1.2 \times 10^{-12}$	
$\text{R} + \text{O}_2 \rightarrow \text{RO}_2$	$6 \times 10^{-12}$ (estimate)	
$\text{R} + \text{Cl}_2 \rightarrow \text{Cl}$	$3 \times 10^{-11}$ (estimate)	
$\text{RO}_2 + \text{RO}_2 \rightarrow$	$5 \times 10^{-12}$ (estimate)	

Note – all rate parameters in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and taken from (Atkinson et al., 2007) unless stated.

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## OH from peroxy radicals

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J. N. Crowley**Table 1.** Determinations of  $\alpha_1$  and corresponding experimental conditions.

<i>P</i> /mBar	[CH <sub>3</sub> OH] <sup>a</sup>	[CH <sub>3</sub> CHO] <sup>a</sup>	[Cl <sub>2</sub> ] <sup>a</sup>	[Cl] <sup>b</sup>	<i>m</i> , [NO] <sup>b</sup>	<i>n</i> , [CH <sub>3</sub> C(O)O <sub>2</sub> ] <sup>b</sup>	$\alpha_1^c$
100	49.0	1.8–3.4	89	580	4, 29–61	3, 29–52	0.55±0.10
207	9.6	0.7	72	440	2, 120	2, 39	0.45±0.10
229	60.8	3.0–5.7	92	610	3, 47–97	2, 39–70	0.5±0.05
230	44.2	1.9–5.0	98	720	4, 27–69	3, 30–72	0.55±0.05
240	33.0	1.7–3.0	86	640	2, 42	2, 43–75	0.55±0.05
250	32.3	1.2–3.2	91	640	4, 17–44	4, 30–76	0.5±0.05
430	41.0	1.6–4.8	78	550	4, 26–67	3, 28–80	0.6±0.15
705	95.1	6.1–8.5	96	590	2, 58–149	2, 47–68	0.45±0.10

## Notes:

<sup>a</sup>=precursor concentrations in units of 10<sup>14</sup> molecule cm<sup>-3</sup>;<sup>b</sup>=radical (Cl, NO, CH<sub>3</sub>C(O)O<sub>2</sub>) concentrations in units of 10<sup>11</sup> molecule cm<sup>-3</sup>;*m*=number of calibration (R4) profiles recorded, over a range of [NO];*n*=number of (R1) profiles used to determine  $\alpha_1$ ;<sup>c</sup>=errors in  $\alpha_1$  account for variability in (R1) or calibration data and do not include the systematic uncertainty (±25%) in initial radical density – see Sect. 3.1 for details.

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**Table 2.** Determinations of OH yield  $\alpha$  for other HO<sub>2</sub>+RO<sub>2</sub> reactions.

HO <sub>2</sub> +	RH	[RH] <sup>a</sup>	n, [RO <sub>2</sub> ] <sup>b</sup>	$\alpha$ <sup>c</sup>
CH <sub>3</sub> C(O)CH <sub>2</sub> O <sub>2</sub> (R2)	CH <sub>3</sub> C(O)CH <sub>3</sub>	32–360	6, 14–110	0.15 <sup>+0.15</sup> <sub>-0.05</sub>
HOCH <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> (R8)	CH <sub>3</sub> CH <sub>2</sub> OH <sup>d</sup>	29–40	6, 51–53	<0.04
CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> (R9)	(CH <sub>3</sub> ) <sub>2</sub> CHOH	4.9–9.6	2, 12–20	<0.06
ClC <sub>5</sub> H <sub>8</sub> O <sub>2</sub> (R33) <sup>e</sup>	C <sub>5</sub> H <sub>8</sub>	0.54	1, 43	<0.04
HOC <sub>5</sub> H <sub>10</sub> O <sub>2</sub> (R34) <sup>f</sup>	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> OH	0.6–1.2	3, 14–26	<0.06
C <sub>6</sub> H <sub>5</sub> C(O)O <sub>2</sub> (R35)	C <sub>6</sub> H <sub>5</sub> CHO	2.0–3.9	2, 47–87	≈0.2
C <sub>2</sub> H <sub>5</sub> C(O)CH <sub>2</sub> O <sub>2</sub> (R36) <sup>g</sup>	CH <sub>3</sub> C(O)C <sub>2</sub> H <sub>5</sub>	8.1–11.5	3, 55–76	≈0.2

## Notes:

all experiments conducted at around  $T=298$  K and  $P=220$  mBar unless stated, see Sect. 3.4 for further details;

<sup>a</sup>= $[RH]$  in units of  $10^{14}$  molecule  $\text{cm}^{-3}$ ;

<sup>b</sup>= $n$  is number of determinations of  $\alpha$ ,  $[RO_2]$  in units of  $10^{11}$  molecule  $\text{cm}^{-3}$ ;

<sup>c</sup>=errors in  $\alpha$  do not include the systematic uncertainty ( $\pm 25\%$ ) in initial radical density;

<sup>d</sup>= $\alpha_8$  determined at  $T=259$ , 298 and 351 K;

<sup>e</sup>=ClC<sub>5</sub>H<sub>8</sub>O<sub>2</sub> refers to 4 isomeric RO<sub>2</sub>;

<sup>f</sup>=HOC<sub>5</sub>H<sub>10</sub>O<sub>2</sub> refers to three isomers;

<sup>g</sup>=C<sub>2</sub>H<sub>5</sub>C(O)CH<sub>2</sub>O<sub>2</sub> refers to three isomers.

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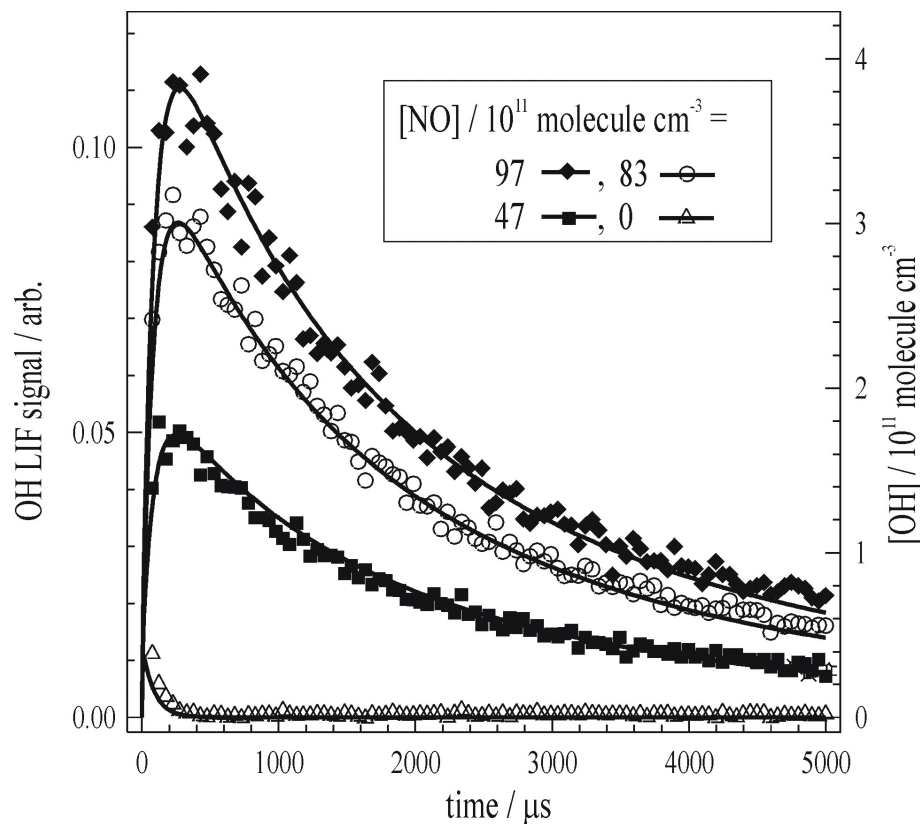
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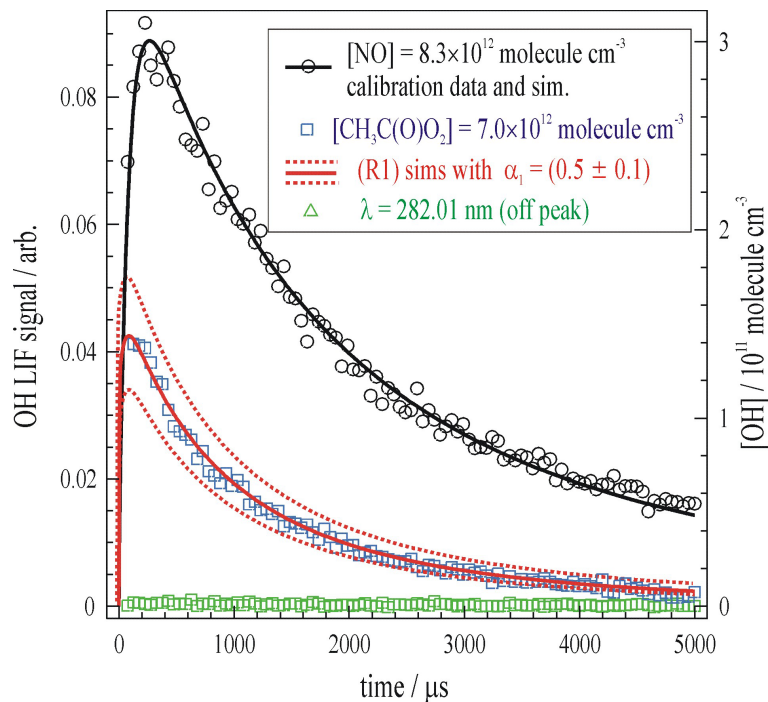
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**Fig. 1.** Calibration of the OH LIF detection system using (R4) ( $\text{HO}_2 + \text{NO}$ ). Generation (R10–R12) of  $[\text{HO}_2] = 6.1 \times 10^{13} \text{ molecule cm}^{-3}$  in the presence of  $[\text{NO}] / 10^{11} \text{ molecule cm}^{-3} = 97$  (solid diamonds), 83 (open circles) and 47 (solid squares) produced these three OH profiles which were subsequently used to determine  $\alpha_1$  (see Fig. 2). Calibration was achieved by matching the LIF signal to that of its corresponding numerical simulation (see Sect. 2.4 for details).

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**Fig. 2.** Experiment to determine the yield of OH,  $\alpha_1$ , for (R1)  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \rightarrow$  (products). The blue squares show the OH LIF signal, observed following generation of  $[\text{CH}_3\text{C}(\text{O})\text{O}_2] = 7.0 \times 10^{12} \text{ molecule cm}^{-3}$  in the presence of  $[\text{HO}_2] = 5.4 \times 10^{13} \text{ molecule cm}^{-3}$ , clearly demonstrating that OH is a major product of (R1). Numerical simulations (in red) show that a yield of  $\alpha \approx 0.5$  was required to reproduce this and similar experimental datasets (see Table 1). Note that when the probe laser was tuned away from the OH line ( $\lambda = 282.01 \text{ nm}$ , green triangles), no fluorescence was detected, indicating that OH and only OH was detected as a product from (R1). These LIF signals were calibrated (R4) using the data presented in Fig. 1. For clarity only one calibration profile is displayed here (open black circles:  $[\text{NO}] = 8.3 \times 10^{12} \text{ molecule cm}^{-3}$ ).

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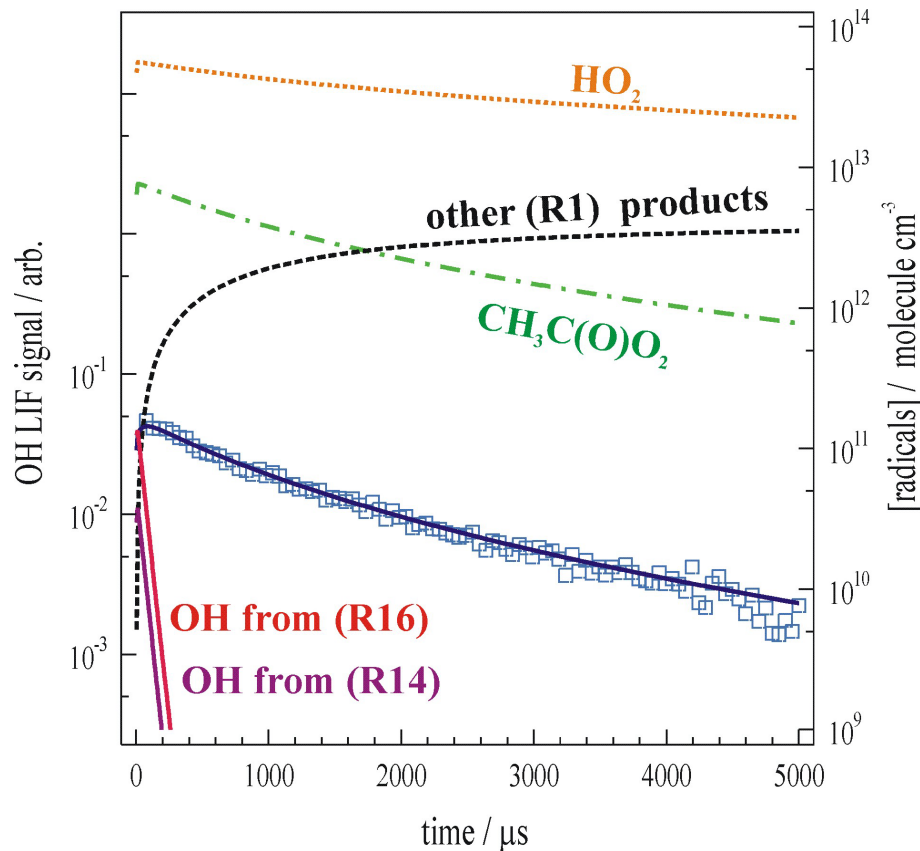
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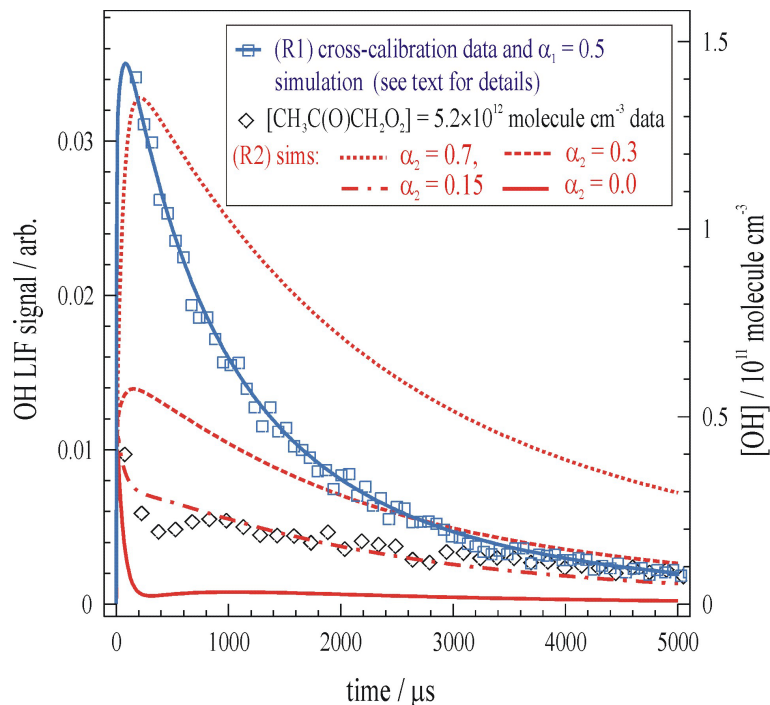
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**Fig. 3.** Numerical simulation of an experiment to determine  $\alpha_1$  (note the logarithmic scale on the y-axes). In blue are the experimental datapoints already displayed in Figure 2, with corresponding simulation using  $\alpha_1=0.5$ . OH profiles resulting from (R14b) and (R16b), simulated here as purple and red solid lines, have very different temporal characteristics to (R1). These reactions were not therefore a major source of error in our determination of  $\alpha_1=0.5$ .

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**Fig. 4.** Experiment to determine the OH yield  $\alpha_2$  for (R2)  $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2 \rightarrow$  (products). The black diamonds represent the OH LIF signal recorded following generation of  $[\text{CH}_3\text{C}(\text{O})\text{O}_2] = 5.2 \times 10^{12} \text{ molecule cm}^{-3}$  in the presence of  $[\text{HO}_2] = 5.8 \times 10^{13} \text{ molecule cm}^{-3}$ . LIF was calibrated by the regular (R4) method (see Sect. 2.4). Back-to-back experiments were also conducted where  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  was replaced by  $\text{CH}_3\text{CHO}$ , and the OH yields from (R2) and (R1) were directly compared. The result (blue square datapoints and solid line depicting  $\alpha_1 = 0.5$ ) confirms that  $\alpha_2$  is indeed significantly smaller than  $\alpha_1$ .

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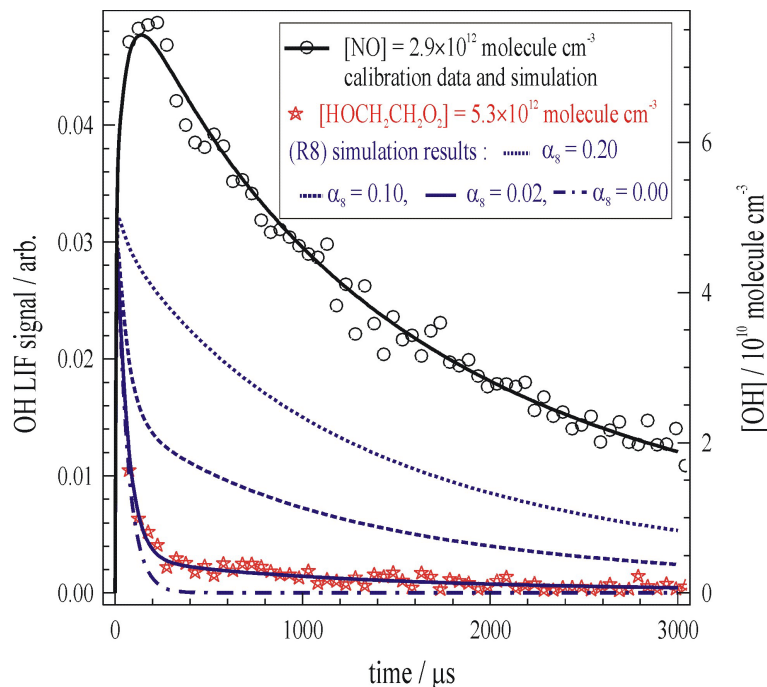
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**Fig. 5.** Experiment to determine  $\alpha_8$  for (R8)  $\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow (\text{products})$ . The open black circles describe data where  $[\text{NO}] = 2.9 \times 10^{12} \text{ molecule cm}^{-3}$  was used to generate a known amount of OH and hence calibrate the LIF detection system. The red stars show data obtained following generation of  $[\text{HOCH}_2\text{CH}_2\text{O}_2] = 5.3 \times 10^{12} \text{ molecule cm}^{-3}$  in the presence of  $[\text{HO}_2] = 5.6 \times 10^{13} \text{ molecule cm}^{-3}$ . Numerical simulation demonstrated that small OH yields of  $\alpha_8 \approx 0.02$  were required to reproduce this and similar datasets (see Sect. 3.3 and Table 2 for details).

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